COATINGS. ENAMELS

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LOW-MELTING TINTED GLASSES FOR DECORATING SHEET GLASS

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Low-melting tinted glasses with a spreading temperature of 550°C are developed in the $ZnB_2O_4 - NaPO_3$ system for decorating sheet glass. Their main physicochemical properties are investigated. Experiments performed in industrial conditions demonstrate positive results in decorating sheet glass by silk-screen printing with subsequent firing at a temperature above 550°C.

Sheet glass products are extensively used in construction and industry, both as functional and decorative elements, therefore, the development of low-melting glasses for sheet glass decoration not containing Pb and Cd is a topical problem [1 – 3]. A series of experiment revealed that glasses of the $ZnB_2O_4 - NaPO_3$ system can be used to produced pigments of various shades with a firing temperature of 550 – 650°C suitable for the decoration of various articles, including those that contact food products [4, 5].

The purpose of our study is to investigate the possibility of obtaining low-melting glass pigments for decorating sheet glass, including the silk-screen printing method.

Glasses were synthesized in a electric furnace with silit heaters at a temperature of 1000 – 1200°C in glass-carbon crucibles. Molding was performed in graphite molds with subsequent annealing in an electric muffle furnace.

The density of obtained samples was measured by hydrostatic weighing with an accuracy of ± 0.001 g/cm^3, the CLTE was measured with a DKV-4 vertical quartz dilatometer in the temperature range of 20 – 600°C, and hydrolytic resistance was determined by the standard method.

The crystallization capacity was studied by the polythermal method in a gradient furnace at a temperature of 500 – 900°C. The spreading temperature was determined within a temperature range from 400 to 600°C with a step of 50°C and a 15 min exposure at each step. The contact wetting angle was measured on a sample fully spread over the substrate with an accuracy of 1°.

Glasses of the $NaPO_3 - ZnB_2O_4$ system were synthesized adding Al_2O_3, SiO_2 and pigments: Co_2O_3, NiO, CuO, MnO, Fe_2O_3, TiO_2, and CeO_2. Zinc metaborate ZnB_2O_4 was introduced into the batch via ZnO and H_3BO_3 taken in a stoichiometric ratio. Based on experiments results, a clear glass with a molar content of 56% ZnB_2O_4 and 44% ($NaPO_3 + Al_2O_3 + SiO_2$) was taken as the reference composition for further studies. Its CLTE is 78×10^{-7} K^{-1} and its vitrification temperature is 460°C.

Tinted glasses were synthesized by the same technology as in clear glass production. A pigment was introduced into the batch above 100 mol.%. The main properties and color shades of glasses are given in Table 1.

The considered glasses are weekly crystallizing at a temperature below 800°C, belong to class I of hydrolytic resistance, and have a spreading temperature of 550°C. The wetting angle of a sample completely spread on a substrate of float glass M1 is equal to 39 – 42° (GOST 111–2001).

A glass for decorating sheet glass should have a CLTE equal or lower by 5 – 7% than the CLTE of the substrate and a spreading temperature lower than the deformation start temperature of the substrate glass. The use of colorants that are traditional applied to silicate glasses demonstrated that borophosphate glasses have different coloring. For instance, Co_2O_3 instead blue or pink color produces a violet tint, whereas NiO instead of yellow or violet produces a brown color.

Thus, low-melting lead-free glasses have been obtained in the $NaPO_3 - ZnB_2O_4$ system and can be used as decorative coatings for sheet glass with a heat treatment temperature of 550°C.

The absence of lead in glass makes it possible to apply these glass to decorating a wide range of glass articles, including those in direct contact with food, which is also helped by class I of hydrolytic resistance.

The use of commonly available glass colorants makes it possible to expand the color range of glasses without resorting to expensive pigments.

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TABLE 1

Glass	Molar content, %						Visual glass characteristic	Density, g/cm^3	CLTE, 10^{-7} K^{-1}	Temperature, °C	
	Co_2O_3	NiO	CuO	MnO_2	TiO_2	CeO_2				vitrification	deformation start
1	0.5	–	–	–	–	–	Violet	2.815	84	478	505
2	–	2.0	–	–	–	–	Brown	2.805	80	490	520
3	0.5	–	0.5	–	–	–	Dark violet	2.758	80	490	510
4*	–	1.0	–	–	–	–	Dark green	2.729	79	475	505
5	–	–	–	0.6	–	–	Clear	2.805	78	455	490
6	–	–	0.5	0.4		–	Light-bluish-green	2.869	81	460	495
7	–	–	0.5	–	–	–	Light blue	2.778	81	477	505
8	–	–	–	2.0	–	–	Brown	2.851	82	485	512
9	–	–	–	–	2.0	1.0	Yellow	2.845	80	490	520
10	–	1.0	–	–		–	Dark green	2.897	78	465	495

* Beside, glass 4 contains 1.0% Fe_2O_3.

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